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Project Summary

ORIGINAL

Modeling of SO_2 Oxidation in Smog

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Smog chamber experiments were conducted to investigate the kinetics of the free radical reactions of SO_2 in smog and the transformation of SO_2 to sulfate under simulated urban and rural atmospheric conditions. Rate constants were derived for three reactions: $SO_2 + HO + M \rightarrow$ SULFATE (60); $SO_2 + HO_2 \rightarrow$ SULFATE (61); and $SO_2 + CH_3O_2 \rightarrow$ SULFATE (64); where $k_{60} = 1600$, $k_{61} < 0.2$, and $k_{64} < 0.8$ ppm^{-1} min^{-1}, respectively. Oxidation of SO_2 by the unstable intermediate HO led exclusively to particulate sulfate. However, even under favorable NO_x conditions, particulate nitrate was not a product. Hydrocarbon mixtures typical of urban environments promoted SO_2 oxidation faster than hydrocarbons selected to represent rural conditions. Maximum SO_2 oxidation rates occurred during periods of peak NO_2 formation. Oxidation rates of SO_2 in aged smog were 25 to 35% of the maximum rates.

Model calculations indicated that the $SO_2 + HO + M \rightarrow$ SULFATE reaction dominated sulfate production from SO_2 in polluted air. The model also indicated that SO_2 oxidation is heavily influenced by solar radiation intensity and pollutant conditions. For clear-sky and a variety of HC-NO_x conditions, maximum SO_2 conversion rates ranged from 3.7 to 7.4%/h.

Models used to simulate free radical reactions in power plant plumes showed that SO_2 oxidation is strongly dependent on plume dispersion rates, as well as on the same parameters governing SO_2 oxidation in ambient air. Although exceptions do occur for certain HC-NO_x conditions, SO_2 oxidation rates in plumes are generally bound by the ambient rates.

This Project Summary was developed by EPA's Enviornmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The widespread distribution of sulfate aerosols in the atmosphere and their associated effects on visibility and precipitation pH (acid rain) are serious environmental concerns in the United States. The Environmental Sciences Research Laboratory of the U.S. Environmental Protection Agency is working to formulate strategies for the effective control of sulfates. One step toward achieving such control is the development of models to predict regional production of sulfate by SO_2 sources. The study summarized here was conducted by Battelle Columbus Laboratories to broaden the information base available on SO_2 reactions and transformations and to provide the Environmental Sciences Research Laboratory with the predictive models necessary for sulfate control.

Oxidation of SO_2 in the atmosphere is considered the primary source of sulfate particulates. The chemical and microphysical processes involved in the gas-to-particulate transformations of oxidation, however, are highly complex.

Despite numerous research efforts to define these processes more clearly, many essential details pertaining to reaction rates and mechanisms are missing. To date, kinetic and mechanistic studies of the elementary gas phase reactions of SO_2 in air have yielded only that all known reactions involving electronically excited states of SO_2 are insignificantly slow in the troposphere and that HO, HO_2, and RO_2 are the only tropospheric species capable of oxidizing SO_2 at substantial rates.

Numerous studies have presented evidence that submicron-radii sulfates are predominantly $(NH_4)_xH_{2-x}SO_4$ with associated water. However, although microphysical aspects of H_2SO_4 particle formation are well understood, much uncertainty surrounds defining new particle nucleation. Some investigators have concluded that SO_2 oxidation in the gas phase is the rate limiting step for the formulation and growth of secondary H_2SO_4 particles in the atmosphere. One objective of this study was to examine these rate limiting reactions.

Finally, based on the new findings and on additional smog chamber data obtained with rural and urban hydrocarbon systems, a photochemical smog model was applied to simulate gas phase SO_2 oxidation rates for various atmospheric conditions.

Procedure

Experiments to investigate the kinetics of the free radical reactions of SO_2 in smog and to obtain data on SO_2 transformation to sulfate under various atmospheric conditions were conducted in Battelle's 17.4 m^3 smog chamber. Rate constants were derived for the following reactions: $SO_2 + HO + M \rightarrow$ SULFATE (60); $SO_2 + HO_2 \rightarrow$ SULFATE (61); and $SO_2 + CH_3O_2 \rightarrow$ SULFATE (64). Pseudo second-order rate constants ($ppm^{-1}\ min^{-1}$) were $k_{60} = 1600$, $k_{61} < 0.2$, and $k_{64} < 0.8$. The values for k_{61} and k_{64} were only upper limit estimates; the rates pertained to the overall conversion of SO_2 to particulate sulfate.

Although the mechanisms of SO_2 conversion were not investigated, some work was done to determine if NO and/or NO_2 form stable aerosol products with the intermediates created after HO addition to SO_2.

Methods for Kinetic Studies

The smog chamber facility has a surface:volume ratio of 0.8 m^{-1}; the surface is polished aluminum (~80%) and FEP Teflon™ (~20%). Irradiation was provided by a bank of 95 fluorescent blacklamps and 15 fluorescent sunlamps. Combined intensity of the lamps yielded a NO_2 photodissociation rate of approximately 0.14 min^{-1}.

Background air for the chamber was passed through a purification system for dehumidification and filtering. SO_2 and NO_2 concentrations were usually below the detection levels of 1 ppb and 2 ppb, respectively. Background NO concentrations ranged from 1 to 2 ppb. Background total hydrocarbon ranged between 1.9 and 2.5 ppmC (of which most was CH_4). Gas chromatographic analyses of background air showed no detectable olefins or aromatics in the C_2-C_9 range when nonmethane hydrocarbon was 0.1 to 0.3 ppmC. When relatively small concentrations of nitrous acid (a source of HO radicals and NO_x) were added to the background air under high molecular weight hydrocarbon contamination, irradiation resulted in peak O_3 concentrations in the 8 to 12 ppb range.

The reactivity of this amount of hydrocarbon contamination in terms of O_3 production corresponds to the reactivity of about 4 to 6 ppm CO. Thus, intentional addition of 4.5 ppmC hydrocarbons and/or large quantities of CH_4 and CO clearly overwhelmed any effects due to background HC contaminants. In addition, intentional introduction of nitrous acid into the air for most of the experiments was thought to overcome any spurious surface contaminant effects which might have led to the generation of free radicals at the outset of irradiation.

Gas phase analyses included measurement of PAN, C_1-C_9 hydrocarbons, CO, O_3, H_2O_2, HNO_2, NO_2, NO_x, NO and SO_2. Initial measurements of SO_2 were taken with a Meloy 285 flame photometer. Upon irradiation, the instrument was used to monitor sulfate aerosol. The photometer was intermittently operated in the total sulfur mode (SO_2 plus sulfate) to check on the SO_2 concentration.

Gas calibrations were performed routinely. The chemiluminescense analyzer used to monitor NO, HNO_2, and NO_2 was spanned before almost every experiment. *In situ* O_3 titrations were conducted in the chamber to check on the span of the O_3 analyzer and the efficiency of the NO_x converters. After an experiment (lamps off), excess NO was injected into the chamber to more than titrate the remaining O_3.

Condensed phase analysis concentrated on the measurement of sulfate aerosol. The primary method for monitoring sulfate was based on continuous sampling by a flame photometric detector (FPD). Checks were made on this method by taking simultaneous large volume collections on quartz filters and comparing the results. Using the tremendous difference in diffusivity between SO_2 and H_2SO_4 aerosols, a diffusion-denuder tube was designed to remove virtually all of the SO_2 in the air sample entering the FPD, while allowing most of the particulate sulfur to pass to the detector. Optimization between maximum SO_2 removal and minimum H_2SO_4 loss was determined experimentally by generating independently known concentrations of SO_2 and H_2SO_4 aerosol in the smog chamber. The optimization work resulted in a sample flow of 200 ml/min through a 35 cm lead acetate diffusion tube, with >99.5% removal of SO_2 and 35% loss of H_2SO_4 aerosol.

Kinetic Data

The objective of the first portion of this project was to investigate the kinetics (and mechanisms where feasible) of SO_2 oxidation by free radicals; namely, HO, HO_2, and CH_3O_2. The approach taken to study these reactions was to generate a variety of distributions, between HO, HO_2, and CH_3O_2 in a smog chamber containing SO_2. This work began with a series of smog chamber experiments using an inorganic smog system ($HNO_2/NO_x/CO/SO_2$). By selecting the initial concentrations of system components, it was possible to affect a range of $HO:HO_2$ ratios and thereby observe the relative rates of SO_2 oxidation attributable to the respective radicals.

To obtain estimates of the free radical concentrations, and hence to calculate absolute rate constants, the experimental data were fitted with a chemical kinetics model. Throughout the study, the SO_2 oxidation rates related to the subject radicals were determined solely in terms of sulfate aerosol product. Any sulfur products remaining in the gas phase were not determined. As such, the rate constants obtained represent rate limiting kinetics for conversion of SO_2 to sulfate and not the upper limit rates for SO_2 removal. In general, good material balances were observed between gas-phase and condensed-phase sulfur, but once the reactions began it

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was not certain that the gas-phase sulfur was exclusively SO_2.

In the inorganic smog system, NO_x (i.e., HNO_2, NO, and NO_2) governed the free radical concentrations because their reaction rates with the radicals were typically orders of magnitude larger than those of the corresponding reactions with SO_2. Thus, before attempting to interpret experimental data pertaining to SO_2 oxidation, the NO_x chemistry as it occurred in the smog chamber had to be investigated. Substantial concentrations of HNO_2 were used as a radical source in many of the experiments.

Three initial experiments were conducted to determine the reaction rates for HNO_2 under experimental conditions and to account for the large NO_x losses observed in most experiments. The first experiment showed that the NO concentration was largely a function of HNO_2's photolysis rate and the HO + NO recombination rate. Material balances between the model and experimental data were reasonably good, although the model slightly underestimated NO_x losses.

The next experiment, conducted to investigate further the smog chamber reactions involving HNO_2 and the formation of HNO_3, investigated two routes for HNO_3 formation in the gas phase: $HNO_2 + O_3 \rightarrow HNO_3 + O_2$ and $N_2O_5 + H_2O \rightarrow 2HNO_3$. The results suggested that neither reaction produced appreciable amounts. The experiments also provided no conclusive data on the HNO_2 photolysis rate in the smog chamber. However the choice of $k = 0.28 \times 10^{-1} min^{-1}$ seemed to fit these and other experimental data as well as alternative values.

The last of these three experiments attempted to measure the reactions involving N_2O_5 formation. Thermal decomposition of N_2O_5 apparently limited its concentrations in the troposphere. The slow rate found for homogenous conversion to HNO_3 coupled to the strong temperature dependence for N_2O_5 decomposition suggested that N_2O_5 persists for substantial periods in the colder regions of the lower atmosphere and that clouds and perhaps moist aerosols may be the dominant sink for N_2O_5.

A series of experiments was also conducted in the inorganic smog system to study the conversion of SO_2 to sulfate via hydroxyl radicals. SO_2 was added to air mixtures of HNO_2 and NO_x in the chamber. Sulfate aerosol formation was observed immediately after the lamps were turned on, and the rate of sulfate formation was generally found to maximize early in the irradiation period and then gradually diminish.

The eight experiments were simulated by kinetic modeling in order to estimate the HO profiles and assess the overall conversion rate for SO_2, as initiated by HO radicals.

Some investigators had suggested that NO_x could have various roles in the transformation process and even become incorporated in the condensed phase as the reactions reached completion. To investigate these hypotheses, various amounts of NO or NO_2 were added to some of the mixtures, in addition to the amounts produced while charging HNO_2 to the chamber.

The model gave satisfactory fits to the experimental data, with only one experiment in the series excepted. The model tended to underestimate NO_2 conversion and sulfate aerosol concentrations, particularly during the latter half of the experimental periods. The discrepancies rarely exceeded 20% of the experimental values, however.

The data supported a rate constant of 1.6×10^3 $ppm^{-1}min^{-1}$ for the conversion of SO_2 to sulfate aerosol, as initiated by the HO radical.

The last series of experiments in the inorganic smog system was conducted to determine the kinetics of SO_2 oxidation by hydroperoxy radicals. To investigate the reactions in the smog chamber, relatively large concentrations of CO were added to mixtures of $NO_x/HNO_2/SO_2$. CO was found to give a negative interference to the analyses of SO_2 and sulfate aerosols with the FPD. This interference severely limited the range of useful CO concentration.

Based on the data from this group of experiments, the selection of an upper limit for the $SO_2 + HO_2 \rightarrow$ SULFATE reaction was arbitrary. Thus for subsequent modeling, 0.2 $ppm^{-1}min^{-1}$ was chosen as a certain upper limit, although the true rate is likely to be much lower.

In the organic smog system, experimenters investigated the methylperoxy-SO_2 reaction beginning with the same approach used for the HO_2-SO_2 kinetics studies. The approach consisted of irradiating high concentrations of CH_4 with controlled $HNO_2/NO_x/SO_2$ mixtures in the smog chamber. The reaction of principal concern was $CH_3O_2 + SO_2 \rightarrow CH_3O$ + SULFATE.

Two initial experiments were undertaken to determine the overall rate of the above reaction based on sulfate aerosol formation in an atmosphere of moderate humidity. Methane was used as the methylperoxy source in the experiments. Although results were inconclusive, an upper limit estimate of 0.8 $ppm^{-1}min^{-1}$ was obtained for the conversion of SO_2 to sulfate via the methylperoxy radical. The mechanism of the conversion was not investigated. Because of the inconclusive results obtained with the $CH_4/HNO_2/NO_x/SO_2$ smog system, additional experiments were conducted using azomethane as the methylperoxy source. However, these experiments too were quite limited.

Role of NO_x in SO_2 Oxidation Via HO Radicals

Experiments conducted with the $HNO_2/NO_x/SO_2$ smog system served to investigate the possibility for particulate nitrate formation. At the conclusion of an experiment, sample air was drawn through acid washed and neutralized quartz filters and analyzed for NO_3^-, $SO_4^=$, and NH_4^+. To avoid HNO_2 or HNO_3 volatilization losses, filter samples were immediately halved; one-half was stored in a desiccatory containing NH_3, and the other was refrigerated without treatment.

The analytical results from nine experiments showed no substantial differences in either $SO_4^=$ or NO_3^- for the NH_3 treated samples versus the untreated samples. Although ammoniated samples contained somewhat higher NH_4^+ concentrations, nearly all samples were deficient in NH_3 when compared to the expected stoichiometry for $(NH_4)_2SO_4$ and NH_4NO_3.

In every case, the particulate nitrate concentrations were very low compared to the sulfate concentrations. The highest particulate nitrate concentrations were recorded for the two experiments without SO_2. Thus a substantial amount of nitrate was not incorporated in the particulate phase under the conditions of these experiments. While the results do not rule out the possibility that $HOSO_2O$ interacts with NO_2 to produce H_2SO_4 and HNO_3, they do indicate that nitrate (if formed via this route) is not maintained in the aerosol phase, even under the presumably stabilizing influence of NH_3.

SO_2 Oxidation in Simulated Urban and Rural Atmospheres

In the second portion of this study, a series of smog chamber experiments

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was conducted to investigate some of the factors affecting SO_2 oxidation under simulated atmospheric conditions and to develop data needed to evaluate photochemical models of SO_2 oxidation in polluted air.

Experiments were conducted using hydrocarbon mixtures selected to represent urban and rural conditions. For each experiment, the initial nonmethane hydrocarbon concentration was about 4.5 ppmC, and the initial NO_x concentration was 0.3 ppm. Apart from the control experiments where no SO_2 was introduced, 0.6 ppm SO_2 was injected into the chamber at either 1 or 5 h intervals after the irradiation began. Replicate experiments were also conducted in which 0.15 ppm NO was injected, together with 0.6 ppm SO_2. This approach was designed to simulate conditions in which SO_2 is emitted into polluted air from point sources. The experimenters attempted to determine whether or not SO_2 oxidation rates depended substantially on the interval of the photochemical smog period, and to what extent the presence of NO (NO is generally emitted along with SO_2) affected the oxidation rates.

Analytical methods for determining SO_2 and sulfate aerosols were identical to those used in the kinetic experiments. For this experimental series, two Meloy sulfur analyzers were used to monitor SO_2 and particulate sulfate simultaneously.

During the period of these experiments, Battelle's large smog chamber was lined with 5 mil FEP Teflon™ filter. The light intensity corresponding to k was 0.17 min^{-1}. Gas chromatographic analyses for hydrocarbons were obtained initially and at irradiation intervals of 1, 3, 5, and 7 h. PAN concentrations were obtained hourly.

For both urban and rural hydrocarbon mixtures, the rates of SO_2 oxidation were greatest near the periods of peak NO_2 formation, and gradually diminished thereafter. After 24 h of irradiation, the rate of SO_2 oxidation was about one-fourth as large as the maximum rate observed with the urban hydrocarbon mix: for the rural hydrocarbon mix, the rate of SO_2 oxidation at 24 h was about one-third the maximum rate.

The addition of NO with SO_2 (at SO_2:NO ratios of 4:1) at different intervals of the irradiation period had mixed results. When added at 5 h, NO had small positive effects on the rates of SO_2 oxidation, but when added at 1 h, NO reduced the rates of SO_2 oxidation.

Kinetic Model Application

One objective of this portion of the study was to determine if a relatively simple model of atmospheric chemistry could suffice to represent SO_2 oxidation in polluted air. The smog chamber data previously presented and some field data from the Midwest Interstate Sulfur Transformation and Transport (MISTT) project provided the basis for applying the model.

In most cases, the predictions for SO_2 conversion to sulfate were reasonably good; within 20% for the inorganic smog systems and within 25% for the HC-NO_x systems. The model tended to underestimate SO_2 conversion. and the hydrocarbon systems when the model estimates were only one-half the actual rates. For the smog conditions that were modeled, it was estimated that at least 75% and sometimes greater than 90% of the SO_2 oxidation was initiated by reactions of SO_2 with HO radicals.

Although several shortcomings of the lumped model were found during its application to these data, it was still of interest to adapt the model to estimate diurnal patterns of SO_2 oxidation in comparison with field data. The objective of this exercise was to estimate the rate of SO_2 oxidation for power plant plumes resident in polluted atmospheres, as a function of solar radiation, plume emission periods, and plume dispersion rates.

According to the modeling results, the production of HO and the oxidation of SO_2 depended strongly on solar radiation intensity. Reduced radiation resulted in disproportionately lower rates of SO_2 oxidation. For reduced radiation conditions, the maximum rates of SO_2 oxidation were predicted to occur near mid-afternoon, while for clear sky conditions, the maximum oxidation rates occurred between 11:00 a.m. and noon. The rates of SO_2 oxidation were shown to depend on ambient HC and NO_x conditions. For the range of conditions modeled, the maximum rate of SO_2 oxidation (clear sky) varied from 3.7 to 7.4%/h.

Plume dispersion rates affected the induction period of NO and SO_2 oxidation. Variations in solar radiation intensity and thus the diurnal period of the power plant emissions strongly affected SO_2 oxidation rates. For well-dispersed plumes and clear sky conditions, maximum SO_2 oxidation rates (ranging from 2.7 to 6.9%/h) were estimated to occur during the noon to early afternoon periods. The patterns of SO_2 oxidation predicted by the model agreed well with the data for the Labadie plume as reported in the MISTT project.

For relatively low HC:NO_x ratios for ambient air, SO_2 oxidation rates computed for plumes were bound by the ambient rates of SO_2 oxidation. At high HC:NO_x ratios, the rates of SO_2 oxidation in plumes were predicted to exceed the rates in ambient air. Under such conditions, the model also predicted an excess (or bulge) in the plume O_3 concentrations. These features have been observed in actual plume studies.

Conclusions and Recommendations

Regarding reaction 60 ($SO_2 + OH + M \rightarrow$ SULFATE), it appears that all of the SO_2 oxidized by this route results in the formation of sulfate particles. According to the analyses for particulate nitrate, they did not form stable aerosol products with the intermediates created after HO addition to SO_2.

In the course of the experiment with inorganic smog systems ($HNO_2/NO_x/SO_2$), additional kinetic information was obtained, particularly as it pertained to the experimental system. An upper limit rate of 3×10^{-7} $ppm^{-1}min^{-1}$ was derived for the homogeneous reaction between dinitrogen pentoxide and water vapor to yield nitric acid ($N_2O_5 + H_2O \rightarrow HNO_3$). It was also determined that ozone and nitrous acid do not react at a significant rate to produce nitric acid. No heterogeneous reaction between SO_2 and nitrous acid in the presence of sulfuric acid aerosols could be detected.

Although the average reactivity for the urban and rural hydrocarbon mixtures, based on rate constants of individual hydrocarbons with HO radicals, was nearly equal, there were marked differences in several important smog parameters. With the urban hydrocarbon mixture, the rates of NO oxidation and xylene disappearance and the maximum rates of SO_2 oxidation were about twice as great as for the rural hydrocarbon mixture. The formation of PAN and other products of NO_2 oxidation were also greater for the experiments with urban hydrocarbon.

Since SO_2 oxidation is dominated by the reaction with hydroxyl radicals, and since this initial reaction is the rate-

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limiting step in SO_2's conversion to sulfate, it follows that relatively simple kinetic models which adequately describe the variations in atmospheric HO should suffice to estimate gas phase SO_2 transformation rates.

Experimental and theoretical simulations of urban and rural atmospheres showed that the rates of SO_2 oxidation are strongly coupled to solar radiation intensity and pollution conditions. Although high concentrations of NO generally suppressed or delayed HO production and SO_2 oxidation, NO_2 inhibited SO_2 oxidation by scavenging HO. Aldehydes, CO, and possibly some hydrocarbons tended to inhibit SO_2 oxidation by converting HO into products which were less efficient in oxidizing SO_2. In general, reactive hydrocarbons served to promote SO_2 oxidation, and the stoichiometry or net flux of HO affected by hydrocarbon degradation appeared to be key to the acceleration of SO_2 oxidation in polluted air.

SO_2 oxidation rates in moderately polluted air or in well-aged air that was once polluted were found for the most part to be 60 to 80% lower than the rates in freshly polluted air.

Modeling results indicated that SO_2 oxidation rates in power plant plumes are highly dependent on plume dispersion rates and are coupled to the same parameters governing SO_2 oxidation in the ambient air. For well-dispersed plumes, most rapid SO_2 conversion was predicted to occur from noon through early afternoon. The accompaniment of NO in plumes generally suppressed HO and the rate of SO_2 oxidation. However, under certain circumstances where high concentrations of reactive HC were mixed into a rapidly-dispersing plume, the rate of SO_2 oxidation was expected to exceed the oxidation rate in ambient air. Under such circumstances, an excess of ozone was also predicted in the plume.

This study pointed out the need for further study in the area of sulfate aerosol formation. In particular, since the overall conversion rate for the $SO_2 + HO_2 \rightarrow$ SULFATE reaction was considerably less in this study than the literature value, it is recommended that additional high-pressure measurements of the reaction be made. Any such effort should include the determination of reaction products.

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The complete report, entitled "Modeling of SO_2 Oxidation in Smog," (Order No. PB 82-101 932; Cost: $13.50, subject to change) will be available only from:
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